BINARY VAPOR-LIQUID EQUILIBRIA OF CARBON DIOXIDE-LIGHT HYDROCARBONS AT LOW TEMPERATURE*

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Vapor-liquid equilibrium data for binary systems containing carbon dioxide: $CO_2-C_2H_6$, $CO_2-C_3H_8$, $CO_2-n-C_4H_{10}$, $CO_2-iso-C_4H_{10}$, $CO_2-C_2H_4$, $CO_2-C_3H_6$ and $CO_2-1-C_4H_8$ were determined by the vapor recirculation method in the low-temperature range ($-41.6°C-0°C$). The $CO_2-C_2H_4$ and $CO_2-C_2H_6$ systems formed minimum-boiling azeotropes. The modified Redlich-Kwong equation of state was used to calculate vapor-liquid equilibria of these systems. It provided fairly good agreement with experiment.

The vapor-liquid equilibrium of carbon dioxide-light hydrocarbons at low temperatures is of interest in the design of the proper equipment to make such separations. In the previous paper[4] of this series, the equilibrium relationships for two binary mixtures of carbon dioxide with ethylene and ethane at 0°C have been described. Those for the ethylene and ethane binaries with carbon dioxide have been shown to form minimum-boiling azeotropes.

We have therefore extended the work to include mixtures of several hydrocarbons with carbon dioxide. The present paper provides the results of experimental investigations of the equilibria in binary systems of carbon dioxide with four light paraffins, i.e. ethane, propane, n-butane and isobutane, and with three light olefins, i.e. ethylene, propylene and 1-butene in the low-temperature range ($-41.6°C-0°C$). Such mixtures are of general interest for two reasons. First, the phase behavior of binary mixtures of carbon dioxide and light hydrocarbons has been investigated in some detail since the measurement of Kuenen[11] in 1897, but there have been few vapor-liquid equilibria studied in the low-temperature range. Of more interest is the fact that these binaries do differ markedly in phase behavior from hydrocarbon systems because of the significant quadrupole moment of carbon dioxide as well as weak acid-base complex formation with hydrocarbons[12] and such complicated behavior prevents us from calculating phase equilibrium with an aid of the equation of state.

Comparison of the experimental data with the results calculated by using the modified Redlich-Kwong equation[9,16] of state was made, and it appeared to provide a fairly good representation of the experimental data for each binary system.

Experimental Apparatus and Methods

The apparatus was the vapor-recycle type described in detail by Hakuta *et al.*[5]. Small changes were made in maintaining a constant low temperature of the bath using liquid nitrogen as the refrigerant.

A schematic diagram of the apparatus is given in **Fig. 1**. The gaseous materials were charged into the glass-windowed equilibrium cell. Vapor recirculation was carried out by means of a specially designed double-acting magnetic piston pump. Vapor was continuously removed from the top of the equilibrium cell and reintroduced at the bottom, where vapor bubbled up through the liquid to establish vapor-liquid contact. After the system was allowed to remain at desired temperature and at constant pressure for at least half an hour, samples of 10 ml from vapor-phase were isolated in the sampling cell between two needle valves attached to the recirculating line,

1. Equilibrium Cell
2. Thermocouple (copper-constantantan)
3. Vapor Phase Sampling Cell
4. Liquid Phase Sampling Cell
5. Magnetic Piston Pump
6. Sample Gas Cylinder
7. Bourdon Pressure Gage
8. Temperature Detector
9. Liquid Nitrogen Thermos Bottle
10. Compressed Nitrogen Cylinder
11. Constant Temperature Bath
12. On-Off Control Valve

G : To Gas Chromatograph
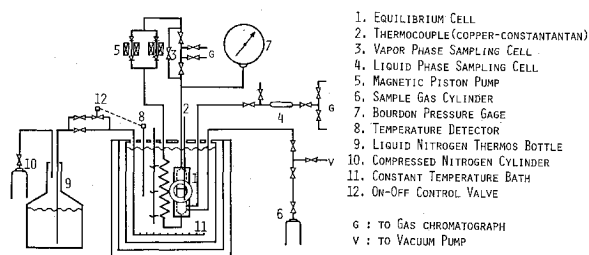V : To Vacuum Pump

Fig. 1 Schematic diagram of vapor-liquid equilibrium apparatus

Table 1 Column condition of gas chromatograph

System	Length [m]	Packing	Flow rate [ml/min]
Carbon dioxide—Ethane	1.8	Polapac Q	40
Carbon dioxide—Propane	1.0	silica gel	70
Carbon dioxide—n-Butane	0.5	silica gel	60
Carbon dioxide—iso-Butane	1.0	silica gel	60
Carbon dioxide—Ethylene	1.8	Polapac Q	32
Carbon dioxide—Propylene	0.7	silica gel	120
Carbon dioxide—1-Butene	0.5	silica gel	100

Table 2 Purity of materials

Carbon dioxide	99.8 % min.
Ethane	99.0 % min.
Propane	99.85% min.
n-Butane	99.35% min.
iso-Butane	99.2 % min.
Ethylene	99.95% min.
Propylene	99.32% min.
1-Butene	99.4 % min.

Table 3 Vapor-liquid equilibrium data for the system carbon dioxide (1)-ethane (2) at −20.2°C

P [atm]	x_1	y_1	K_1	K_2	α_{12}
14.1	0.0	0.0	—	1.0	—
15.9	0.055	0.133	2.418	0.918	2.636
17.3	0.102	0.220	2.157	0.869	2.483
18.7	0.163	0.309	1.896	0.826	2.296
19.9	0.234	0.373	1.594	0.819	1.948
21.1	0.325	0.445	1.369	0.822	1.665
21.6	0.384	0.503	1.310	0.807	1.624
22.3	0.508	0.570	1.122	0.874	1.284
22.6	0.577	0.613	1.062	0.915	1.161
22.7	0.600	0.621	1.035	0.948	1.092
22.8	0.659	0.663	1.006	0.988	1.018
22.7	0.745	0.714	0.954	1.122	0.851
22.0	0.863	0.803	0.931	1.438	0.647
20.8	0.945	0.898	0.950	1.855	0.512
19.3	1.0	1.0	1.0	—	—

Table 4 Vapor-liquid equilibrium data for the system carbon dioxide (1)-propane (2)

P [atm]	x_1	y_1	K_1	K_2	α_{12}
Temp=0°C					
4.7	0.0	0.0	—	1.0	—
5.5	0.013	0.127	10.045	0.885	11.359
7.3	0.034	0.330	9.666	0.694	13.926
10.2	0.086	0.523	6.146	0.515	11.945
14.7	0.176	0.674	3.829	0.396	9.664
18.9	0.291	0.745	2.563	0.360	7.129
24.4	0.461	0.828	1.796	0.319	5.627
27.4	0.622	0.859	1.382	0.371	3.772
29.8	0.719	0.893	1.242	0.381	3.262
32.0	0.840	0.929	1.105	0.445	2.483
33.9	0.953	0.976	1.025	0.498	2.059
34.4	1.0	1.0	1.0	—	—
Temp=−20.2°C					
2.4	0.0	0.0	—	1.0	—
3.3	0.030	0.313	10.433	0.708	14.732
4.5	0.055	0.513	9.327	0.515	18.100
6.2	0.125	0.661	5.288	0.387	13.650
7.7	0.177	0.723	4.085	0.337	12.136
9.6	0.246	0.776	3.154	0.297	10.616
11.1	0.322	0.811	2.519	0.279	9.035
12.8	0.401	0.845	2.107	0.259	8.141
14.6	0.544	0.878	1.614	0.268	6.034
16.4	0.694	0.906	1.305	0.307	4.248
18.1	0.868	0.951	1.096	0.371	2.953
19.3	1.0	1.0	1.0	—	—

Table 5 Vapor-liquid equilibrium data for the system carbon dioxide (1)-n-butane (2) at 0°C

P [atm]	x_1	y_1	K_1	K_2	α_{12}
1.04	0.0	0.0	—	1.0	—
2.4	0.030	0.588	19.600	0.425	46.150
3.9	0.057	0.741	13.000	0.275	47.324
5.8	0.094	0.826	8.787	0.192	45.742
8.3	0.144	0.877	6.042	0.152	39.776
10.6	0.200	0.900	4.500	0.125	36.000
12.9	0.275	0.916	3.330	0.117	28.732
15.3	0.334	0.920	2.754	0.120	22.931
17.8	0.398	0.932	2.342	0.113	20.726
20.0	0.469	0.942	2.009	0.109	18.397
22.9	0.568	0.951	1.674	0.113	14.762
25.7	0.681	0.963	1.414	0.116	12.190
28.6	0.804	0.974	1.211	0.133	9.126
31.5	0.911	0.983	1.079	0.191	5.649
34.4	1.0	1.0	1.0	—	—

Table 6 Vapor-liquid equilibrium data for the system carbon dioxide (1)-iso-butane (2) at 0°C

P [atm]	x_1	y_1	K_1	K_2	α_{12}
1.55	0.0	0.0	—	1.0	—
2.7	0.022	0.422	19.182	0.591	32.456
3.5	0.037	0.541	14.622	0.477	30.654
4.2	0.038	0.623	16.395	0.392	41.823
5.1	0.053	0.690	13.019	0.327	39.813
6.2	0.073	0.744	10.192	0.276	36.928
7.4	0.098	0.783	7.990	0.241	33.154
8.4	0.149	0.800	5.369	0.235	22.847
9.8	0.166	0.830	5.000	0.204	24.510
11.7	0.224	0.863	3.853	0.177	21.768
14.6	0.317	0.877	2.767	0.180	15.372
16.5	0.378	0.899	2.378	0.162	14.679
17.4	0.403	0.913	2.266	0.146	15.510
18.1	0.416	0.914	2.197	0.147	14.946
21.1	0.513	0.922	1.797	0.160	11.231
23.5	0.598	0.925	1.547	0.187	8.273
26.1	0.697	0.947	1.359	0.175	7.766
29.1	0.817	0.963	1.179	0.202	5.837
32.0	0.917	0.981	1.070	0.229	4.672
34.4	1.0	1.0	1.0	—	—

and then the liquid-phase sample was expanded into a previously evacuated sampling vessel (volume approximately 10 m*l*) through a capillary tube which extended to the bottom of the equilibrium cell. Before completion of liquid sampling, the liquid-phase capillary had been purged with liquid phase several times to obtain the true equilibrium composition.

The gas- or liquid-phase sample was introduced into the sample loop of a gas chromatograph and then blended to establish a completely homogeneous mixture. A Yanagimoto GCG–3DH gas chromatograph was used for analysis, employing hydrogen as the carrier gas at 40°C. The recorder used with it was a Hitachi QPD–33 (full span 1 mv). At least three analyses were made for each phase. Other analysis conditions for each system are given in **Table 1**.

The controlled-temperature bath is as shown schematically in Fig. 1. The bath consists of a outer evacuated wall and an inner shell completely surrounded by Parlite insulation. Below 0°C the bath

Table 7 Vapor-liquid equilibrium data for the system carbon dioxide (1)-ethylene (2)

P [atm]	x_1	y_1	K_1	K_2	α_{12}
Temp. = −20.2°C					
24.90	0.0	0.0	—	1.0	—
25.15	0.071	0.072	1.014	0.999	1.015
25.50	0.127	0.136	1.071	0.990	1.082
25.65	0.175	0.183	1.046	0.990	1.057
25.85	0.314	0.302	0.962	1.018	0.945
25.80	0.362	0.347	0.959	1.024	0.937
25.60	0.466	0.433	0.929	1.062	0.848
25.35	0.506	0.461	0.911	1.091	0.835
25.25	0.547	0.499	0.912	1.106	0.825
24.30	0.676	0.604	0.894	1.222	0.732
23.40	0.767	0.685	0.893	1.352	0.661
22.45	0.829	0.759	0.916	1.409	0.650
21.75	0.887	0.820	0.925	1.593	0.581
20.65	0.940	0.895	0.952	1.750	0.544
19.30	1.0	1.0	1.0	—	—
Temp. = −41.6°C					
13.60	0.0	0.0	—	1.0	—
13.85	0.079	0.084	1.063	0.995	1.068
14.00	0.176	0.178	1.011	0.998	1.013
13.95	0.275	0.265	0.964	1.014	0.951
13.80	0.413	0.365	0.884	1.082	0.817
13.50	0.510	0.438	0.859	1.147	0.749
13.15	0.572	0.502	0.870	1.177	0.739
12.45	0.735	0.615	0.837	1.453	0.576
11.70	0.833	0.720	0.864	1.677	0.515
10.80	0.914	0.819	0.896	2.105	0.426
10.30	0.948	0.885	0.934	2.212	0.422
9.40	1.0	1.0	1.0	—	—

Table 8 Vapor-liquid equilibrium data for the system carbon dioxide (1)-propylene (2)

P [atm]	x_1	y_1	K_1	K_2	α_{12}
Temp. = 0°C					
5.8	0.0	0.0	—	1.0	—
6.7	0.014	0.119	8.693	0.893	9.734
7.9	0.050	0.274	5.525	0.764	7.229
9.2	0.079	0.352	4.444	0.704	6.316
11.5	0.123	0.493	4.014	0.578	6.943
14.3	0.225	0.614	2.729	0.498	5.483
14.9	0.231	0.630	2.726	0.481	5.667
16.6	0.277	0.662	2.390	0.468	5.112
18.1	0.324	0.715	2.206	0.422	5.232
20.7	0.408	0.772	1.890	0.386	4.896
23.9	0.539	0.821	1.523	0.388	3.930
27.8	0.703	0.880	1.251	0.406	3.082
29.9	0.797	0.914	1.147	0.423	2.712
31.6	0.853	0.940	1.102	0.411	2.681
32.1	0.877	0.946	1.079	0.437	2.472
33.0	0.924	0.962	1.041	0.498	2.091
34.4	1.0	1.0	1.0	—	—
Temp. = −20.2°C					
2.97	0.0	0.0	—	1.0	—
4.5	0.076	0.404	5.316	0.645	8.242
6.2	0.153	0.593	3.876	0.481	8.058
8.0	0.244	0.675	2.766	0.430	6.433
10.2	0.354	0.761	2.150	0.370	5.811
11.8	0.440	0.804	1.827	0.350	5.220
13.7	0.543	0.846	1.558	0.337	4.623
15.8	0.704	0.902	1.281	0.331	3.870
17.7	0.846	0.941	1.112	0.383	2.903
19.3	1.0	1.0	1.0	—	—

Table 9 Vapor-liquid equilibrium data for the system carbon dioxide (1)-1-butene (2) at 0°C

P [atm]	x_1	y_1	K_1	K_2	α_{12}
1.25	0.0	0.0	—	1.0	—
3.1	0.059	0.616	10.441	0.408	25.584
5.6	0.123	0.784	6.374	0.246	25.879
8.1	0.199	0.840	4.221	0.199	21.126
10.8	0.276	0.881	3.192	0.164	19.416
13.7	0.362	0.909	2.511	0.143	17.609
16.5	0.454	0.919	2.024	0.148	13.639
19.3	0.544	0.932	1.713	0.149	11.489
22.1	0.617	0.947	1.535	0.138	11.091
25.4	0.743	0.960	1.292	0.156	8.303
28.7	0.836	0.971	1.161	0.177	6.623
31.5	0.921	0.985	1.069	0.190	5.629
34.4	1.0	1.0	1.00	—	—

fluid, ethanol, was agitated by a stirrer driven by a motor. Liquid nitrogen was the bath refrigerant, entering the system from a pressurized supply dewar through copper tubing. The nitrogen passed through a perforated tube and bubbled through the bath fluid. The temperature control system consisted of glass tube temperature-detector, D.C. amplifier, two manually adjusted needle valves and an on-off control valve driven electrically. The temperature detector was composed of a glass tube thermometer employing black-colored toluene as the enclosed liquid and a phototransister level detector mounted on the thermometer. The difference between the level setting of the detector and the temperature in the bath served as an error signal which was sent to a D.C. amplifier that provided electrical power to the control valve.

Automatic temperature control could be attained only by regulating refrigerant flow rate so as to balance the addition of heat from the surroundings. The measurement at 0°C was taken with ice and water which was agitated vigorously.

Temperature was determined with a caliblated copper-constantan thermocouple in the wall of the cell. The probable error in temperature measurement, due to gradients in the bath, was ±0.05°C.

The pressure in the system was indicated by a Bourdon-tube gage (0–100 atm, 300 mm o.d.) calibrated against a dead-weight gage. The accuracy of the gage is 0.2% of the full-scale reading.

Materials

The pure components used in this study were furnished by Takachiho Chemical Industry Co. Before the materials were used, the analyses were checked by gas chromatography and found to be within the specifications from the supplier in **Table 2**.

Results

Experimental vapor-liquid equilibrium data for the systems carbon dioxide-ethane, carbon dioxide-propane, carbon dioxide-n-butane, carbon dioxide-isobutane, carbon dioxide-ethylene, carbon dioxide-propylene and carbon dioxide-1-butene are presented in **Tables 3** to **9**, respectively and graphical illustrations for some representative systems are shown in
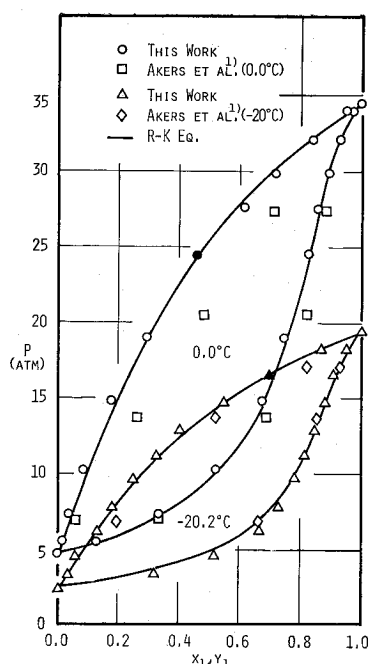
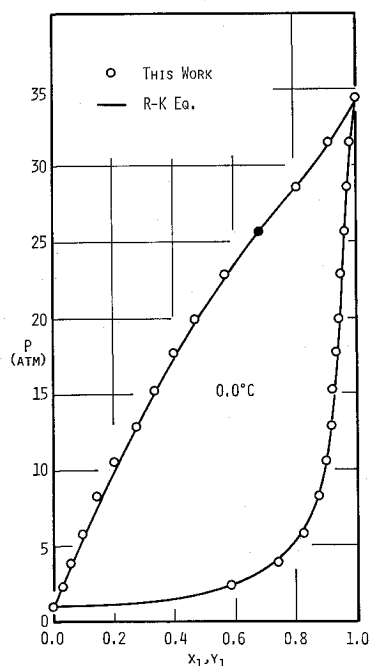Fig. 2 Pressure-composition diagram for the system carbon dioxide (1)-propane (2)

Fig. 3 Pressure-composition diagram for the system carbon dioxide (1)-n-butane at $0°C$
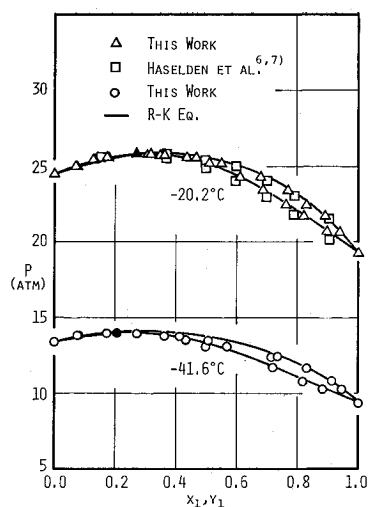

Fig. 4 Pressure-composition diagram for the system carbon dioxide (1)-ethylene (2)

Fig. 5 Pressure-composition diagram for the system carbon dioxide (1)-propylene (2)

Figs. 2 to 5. Through these figures solid lines show the calculated values by using the modified Redlich-Kwong equation of state, which will be mentioned below. The data available from the literature in the temperature range of this investigation are also plotted for each system.

The carbon dioxide-ethane system and the carbon dioxide-ethylene system in Fig. 4 show marked positive deviation from Raoult's law and indicate a maximum in the equilibrium pressure for each iso-

therm. In other words, a low-boiling azeotrope is formed throughout the temperature region investigated.
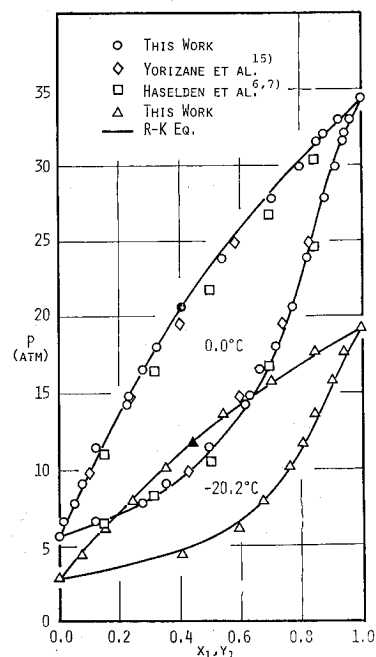
This is in agreement with the results of Hakuta et al.[4], Haselden et al.[6,7] and Clark and Din[3] for carbon dioxide-ethylene and with those of Hakuta et al.[4] and Buckingham[2] for the carbon dioxide-ethane system. The azeotropic composition and pressure determined by plotting the equilibrium ratio against liquid composition and against equilibrium pressure, respectively, are summarized with the literature values in **Table 10**.

Except for the binary systems described above, no tendency toward azeotropic behavior was found in this investigation. In several systems of carbon

dioxide with light hydrocarbons (Figs. 2, 3 and 5), there is apparently a reverse curvature in the vapor lines of each isotherm in the region of rich carbon dioxide content. Akers et al.[1] reported the carbon dioxide-propane system over the temperature range of $-40°F$ to $32°F$ (Fig. 2). The pressure-composition data of this investigation at $-20.2°C$ and those of Akers et al.[1] at $-20°C$ agree comparatively well, but the $0°C$ isotherms show significant deviations, especially on the liquid lines. For the carbon dioxide-propylene system, the present data are compared with literature values in Fig. 5. Haselden et al.[6,7] measured the dew and bubble point curves for this binary over the temperature range of $-30°C$ to $85°C$. Both their interpolated data and the results of Yorizane et al.[15] are in close agreement with the pressure-composition curves obtained in this investigation.

No vapor-liquid equilibrium data for the carbon dioxide-C_4-hydrocarbon systems in the low-temperature region have been reported. A graphical illustration of pressure-mole fraction behavior is given in Fig. 3 for the system carbon dioxide-n-butane. Simillar pressure-composition behavior was obtained for carbon dioxide-isobutane and carbon dioxide-1-butene systems.

In **Fig. 6**, the equilibrium ratio for carbon dioxide is plotted on logarithmic paper at constant temperature $(0°C)$ against pressure. The straight line shows the calculated values by utilizing Raoult's law.

The modified Redlich-Kwong equation of state was used to calculate vapor-liquid equilibria of binary systems which were determined in this investigation. The calculation presented hereinafter follows a method similar to that employed by Peter and Wenzel[13]. The Redlich-Kwong equation modified by Joffe et al.[9], is given as follows:

$$P = RT/(v-b) - a/\{T^{0.5}v(v+b)\} \quad (1)$$

where

$$a_{ii} = \Omega_{ai}R^2T_{ci}^{2.5}/P_{ci} \quad (2)$$

$$b_i = \Omega_{bi}RT_{ci}/P_{ci} \quad (3)$$

and

$$a = \sum_i^n \sum_j^n x_i x_j a_{ij} \quad (4)$$

$$b = \sum_i^n b_i x_i \quad (5)$$

$$a_{ij} = a_{ji} = (1-\theta)\sqrt{a_{ii}a_{jj}} \quad (6)$$

Here the dimensionless parameters for a pure substance Ω_{ai} and Ω_{bi} are given not from critical data but from pure-component volumetric data for the saturated liquid[9]. θ is a interaction parameter which is determined by adjusting it to only one experimental point on the pressure-liquid composition curve of the

Table 10-1 Azeotropic data for the system carbon dioxide (1)-ethane (2)

Temp. [°C]	Pres. [atm]	$x_{1, az}$	Reference
0.0	39.3	0.673	Hakuta et al.[4]
−20.2	22.8	0.666	This work

Table 10-2 Azeotropic data for the system carbon dioxide (1)-ethylene (2)

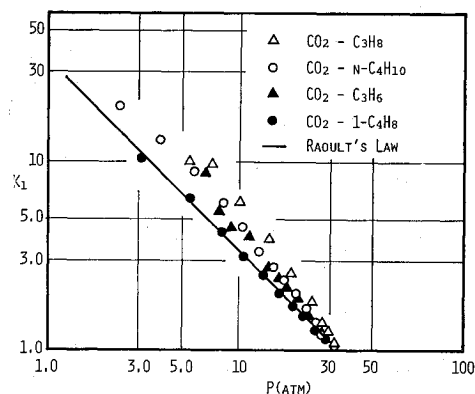| Temp. [°C]	Pres. [atm]	$x_{1, az}$	Reference
0.0	43.4	0.414	Hakuta et al.[4]
0.0	43.18	0.359	Haselden et al.[6]
−10.0	33.00	0.314	ibid.
−20.0	26.06	0.280	ibid.
−20.2	25.85	0.265	This work
−30.0	19.80	0.246	Haselden et al.[6]
−35.0	17.18	0.228	ibid.
−41.6	14.0	0.205	This work

Fig. 6 Equilibrium ratio of carbon dioxide-pressure diagram for the system carbon dioxide (1)-hydrocarbon (2) at 0°C

binary mixture. Applying Eq. (1) to liquid phase as well as vapor phase coupled with a set of parameters for a given temperature, we calculated vapor composition and pressure for each experimental liquid composition and temperature.

The solid lines in Figs. 2 to 5 show the calculated results by using the modified Redlich-Kwong equation mentioned above. The point marked with a solid circle in the plot was taken for the determination of the interaction parameter θ. The calculated results are compared in **Table 11** with the experimental values in this investigation. The binary interaction coefficient θ for each system is also given in this Table. According to the results of Fig. 6 described in the previous section and Table 11, it is seen that the magnitude of θ is, on the whole, corresponding to the extent of the deviation from Raoult's law.

Previously, Joffe and Zudkevitch[8], and Kaminishi et al.[10] have noted that vapor-liquid equilibrium relationships for systems containing carbon dioxide and light hydrocarbons could not be well calculated by using an equation of state. However, it has been pointed out[10,14] that a marked improvement in these calculations was obtained by applying a modified

Component (2)	t [°C]	θ	ΔP [atm]	Δy_1	No. of data points
Ethane	−20.2	0.1271	0.245	0.0083	13
Propane	0.0	0.1532	0.410	0.0102	10
	−20.2	0.1221	0.172	0.0089	10
n-Butane	0.0	0.1083	0.276	0.0108	13
iso-Butane.	0.0	0.1019	0.316	0.0135	18
Ethylene	−20.2	0.0639	0.161	0.0080	13
	−41.6	0.0683	0.171	0.0135	10
Propylene	0.0	0.1030	0.231	0.0101	15
	−20.2	0.0711	0.176	0.0134	8
1-Butene	0.0	0.0579	0.180	0.0098	11

$$\Delta f = \sum_i^N |f_{cal} - f_{exp}|_i / N; \quad N = \text{No. of data points}$$

Benedict-Webb-Rubin equation of state with the correction factor m corresponding to the interaction parameter θ in this investigation. Throughout the carbon dioxide-light hydrocarbon binaries given in Table 11, the overall average deviation of vapor composition is ±0.0097 mole fraction and that of pressure is ±0.212 atm. In particular, the magnitude of deviation in the calculated vapor composition is as small as the results obtained by means of empirical relationships for the activity coefficients.

As discussed above, the modified Redlich-Kwong equation provided a fairly excellent representation of the equilibrium data for the binary mixtures of carbon dioxide-light hydrocarbons at low temperature, and it permitted mixture behavior to be estimated solely from pure-component information and only one experimental datum of the mixture.

Acknowledgment

Nomenclature

a	= constant in the Redlich-Kwong equation	$[l^2 \cdot \text{atm} \cdot °\text{K}^{0.5}/\text{g-mol}^2]$
b	= constant in the Redlich-Kwong equation	$[l/\text{g-mol}]$
K	= vapor-liquid equilibrium ratio	[—]
n	= number of components	[—]
P	= pressure	[atm]
R	= gas constant, 0.082057	$[l \cdot \text{atm/g-mol} \cdot °\text{K}]$
t	= temperature	[°C]
T	= absolute temperature	[°K]
v	= molar volume	$[l/\text{g-mol}]$
x	= mole fraction in liquid phase	[—]
y	= mole fraction in vapor phase	[—]
α	= relative volatility defined as $\alpha_{ij} = K_i/K_j$	[—]
θ	= binary interaction parameter in Eq. (6)	[—]
Ω	= dimensionless constant in Eqs. (2) and (3)	[—]

⟨Subscripts⟩

az	= azeotropic point	
c	= critical state	
i, j, 1 or 2	= component i, j, 1 or 2	
ij	= binary pair of components i and j	

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